MAT-88-02

Hydrogen Evolution and its Effect on High Strength Steel in Concrete

Ontario

Ministry of Transportation

Research and Development Branch

89-03219

Technical Report Documentation Page

Hydrogen Evolution and its Effect on High Strength Steel in Concrete

Author:	S.H. Lo, Ontario Research Foundation
Number:	MAT-88-02
Date of Publication:	August 1988
Ministry Contact:	Hannah Schell, Materials Research Office (416) 235-4693
Abstract:	The long-term performance of concrete highway structures is often affected by the corrosion of embedded reinforcing steel members. Among the various forms of corrosion, the most detrimental form which would lead to a catastrophic failure of a structure without warning is hydrogen embrittlement. In the case of high strength prestressing steel in concrete, the availability of hydrogen is derived mainly from two sources: 1) hydrogen released in the cathodic reactions of corroding steel in concrete; 2) hydrogen generated through the application of cathodic protection. In view of the above, it is pertinent to understand the susceptibility of highway structures to hydrogen embrittlement. In this report, based on the published information, the mechanisms of corrosion, especially hydrogen embrittlement, are discussed. The effects of hydrogen on steel in concrete, with and without externally applied currents are reviewed. An assessment of risks of hydrogen embrittlement in highway structures, with and without cathodic protection, is provided.
Comments:	Final report of Research and Development Branch Project 22185 conducted under the Ontario Joint Transportation Research Program
Key words:	hydrogen evolution, hydrogen embrittlement, high strength steel, prestressed/post-tensioned steel, corrosion, cathodic protection
Distribution:	MTO Head Office and Regions, Municipalities, other Highway Agencies
Copyright Status:	Crown copyright © 1988 Ministry of Transportation

MAT-88-02

Hydrogen Evolution and its Effect on High Strength Steel in Concrete

S.H. Lo
Ontario Research Foundation

Published by
The Research and Development Branch
Ministry of Transportation of Ontario
Hon. Ed Fulton, Minister
D.G. Hobbs, Deputy Minister

Published without prejudice as to the application of the findings.
Crown copyright reserved; however, this document may be reproduced for non-commercial purposes with attribution to the Ministry.

For additional copies, contact:
The Editor, Technical Publications
Room 320, Central Building
1201 Wilson Avenue
Downsview, Ontario
Canada M3M 1J8

Telephone: (416) 235-3480
CNCP Dialcom Electronic Mail: 23:MIN006

August 1988

Table of Contents

1. Introduction 1

2. Background 2
2.1 Background 2
2.2 Stress Corrosion Cracking and Hydrogen Embrittlement 4

3. Factors Influencing Hydrogen Related Corrosion of Steel in Concrete 9
3.1 Mechanical and Metallurgical Factors 9
3.2 Environmental Factors 14

4. Failures Due to the Effect of Hydrogen on Steel in Concrete 19

5. Cathodic Protection of Steel in Concrete 23
5.1 Principles of Corrosion of Steel in Concrete 23
5.2 Cathodic Protection of Prestressed Steel 27

6. Conclusions and Recommendations 31
6.1 Mechanical and Metallurgical 31
6.2 Environmental 32
6.3 Cathodic Protection 34

References 36

Figures (12) 40

Appendices 52
A. Stress Corrosion Cracking 52
B. Hydrogen Embrittlement 62
C. Material Properties of Prestressing Steels 67

Glossary 69

1. INTRODUCTION

The long term performance of concrete highway structures is often affected by the corrosion of embedded reinforcing steel members. Among the various forms of corrosion, the most detrimental form which would lead to a catastrophic failure of a structure without warning, is hydrogen embrittlement. In the case of high strength prestressing steel in concrete, the availability of hydrogen is derived mainly from two sources:

(1) hydrogen released in the cathodic reactions of the corrosion of steel in concrete;

(2) hydrogen generated through the application of cathodic protection.

In view of the above, it is pertinent to understand the susceptibility of highway structures to hydrogen embrittlement

In this report, based on the published information, the mechanisms of corrosion, especially hydrogen embrittlement, are discussed. Further, the effects of hydrogen on steel in concrete, with and without externally applied currents are reviewed. Finally, an assessment of risks of hydrogen embrittlement in highway structures, with and without cathodic protection, is provided.

2. BACKGROUND

2.1 Steel in Concrete

Concrete is a distinctive material which is a combination of coarse and fine aggregates (rock and sand, respectively) and a hardened cement paste. The solid material contains numerous pores which typically make up approximately 20% of its volume. Consequently, concrete has a finite permeability and it must be presumed that components of the surrounding electrolyte are able to penetrate to the steel-concrete interface. In this case, moist concrete exposed to the atmosphere may be envisioned as an electrolyte.

In general, steel in concrete is passivated due to the alkaline nature of the soluble components in the concrete, with the result that the pH is in the range of 12-13. The highly alkaline environment in concrete, results in the formation of a tightly adherent film which passivates the steel and protects it from corrosion. In most cases, concrete is formulated to have a low permeability which minimizes the penetration of corrosion-inducing substances. However, corrosion of steel can occur if the concrete is not of an adequate quality, or the structure is not properly designed for the service environment, or the environment is changed during the service life of the concrete.

The most probable form of corrosion, for steels embedded in concrete, is stress corrosion cracking. The simultaneous presence of tensile stresses (due either to external loading or to internally induced stresses), and known corrosive agents such as nitrates, chlorides, and others, causes this corrosion.

A similiar potential for the corrosion of steel exists when gases such as SO_2, H_2S and NO_2 are present. Carbonization of the concrete by carbon dioxide is another reason for its reduced protective ability. The products of corrosion, and the surface uneveness of steel may reduce the cohesive strength of the steel with concrete and may even play a role in initiating cracks resulting in hazardous brittle failure, especially with high strength steels.

With the above as possible causes of corrosion, protective measures have become necessary to mitigate corrosion and one of these measures involves the application of cathodic protection. However, the criteria for adequate protection, which have been or are currently being utilized in this application are derived mainly from experience with coated steel in soil, or from steel in sea water. In retrospect, the environment which reinforcing steel experiences in chloride-contaminated concrete is sufficiently different from either of the two previous environments that the criteria applied for protection may not be adequate. In particular, one important aspect to be addressed, is the application of a proper polarization potential. Over-protection would lead to hydrogen evolution in steel, which in turn would lead to a more detrimental form of corrosion - hydrogen embrittlement.

This phenomenon is a process in which hydrogen is diffused into a metallic matrix and the mechanical properties of the material are degraded without any chemical reaction taking place between hydrogen and any of the material's components. The continuous diffusion and accumulation of hydrogen into sites of the material structure, result in a drop in local cohesive strength, with the possible initiation of cracks. The sulphide inclusions in steel and also the calcium sulphate of concrete can promote the creation of hydrogen sulphide in wet concrete, which may be the source and stimulus for hydrogen saturation.

2.2 Stress Corrosion Cracking and Hydrogen Embrittlement

The phenomena of stress corrosion cracking and hydrogen embrittlement are very similar in the sense that both give rise to sudden fractures usually unattended by any deformation at all, but the processes leading up to them are fundamentally different in the two cases. Stress corrosion is often regarded as an anodic process whereas hydrogen embrittlement is a cathodic process.

The various models of stress corrosion cracking, describing a premature cracking under the simultaneous action of a corrosion and a tensile stress, can be largely divided into two basic classes. The first class of models considers that crack propagation proceeds by anodic dissolution at the crack tip (dissolution models); while the second class considers that crack propagation is essentially mechanical.

Basically, the slip step dissolution model (Appendix A), describes a situation where crack propagation is achieved by the dissolution of metal at the crack tip, as a consequence of the rupture of otherwise protective surface films by applied stress. Figure 1a schematically shows stress corrosion cracking wherein crack propagation is presumed to occur by anodic dissolution along a pre-existing susceptible path in the metal.

Other models postulate that the crack propagation is achieved by the dissolution of film-free metal due to an increase in the number of active sites provided by plastic deformation at the crack tip[1]; or crack propagation is achieved by the repeated formation and rupture of a brittle film growing into the metal at the crack tip, as first described by Forty[2].

In the case of hydrogen embrittlement, the presence or absence of a surface film may influence the amount of hydrogen adsorbed by the metal. Since the film could provide a surface with characteristics for hydrogen evolution which are significantly different from those of the underlying metal, it will either assist or obstruct the process of hydrogen evolution. The film could constitute a barrier to the migration of hydrogen atoms from an external environment to the substrate metal.

Consequently, the kinetics of hydrogen assisted crack initiation in steels are governed by the combined effects of chemical and mechanical driving forces. The kinetics mainly involve the individual processes in the transport of hydrogen from the gas or liquid phase through the surface layer to the point of crack initiation in the matrix. It should be noted that in regions near a notch root, the applied mechanical stress may enhance the kinetics of the hydrogen transport. The reason is that the configuration at a crack tip differs markedly from that of a flat and unstressed surface. Film formation and adsorption kinetics differ accordingly. The high strain in the atomic bonds, causes a change in the adsorption energies of foreign atoms and molecules, which affects the hydrogen transport kinetics.

The adsorption process of hydrogen in steel has often been regarded as a critical part of the hydrogen embrittlement kinetics. The initiation or continuation of crack growth depends on the rate of accumulation of a critical concentration of hydrogen. It is believed that these kinetics are controlled by surface adsorption [3, 4] phenomena. In principle, figure 1b shows hydrogen embrittlement is controlled by production and adsorption of atomic hydrogen into the metal at cathodic sites followed by a hydrogen-induced brittle failure.

The proposed mechanisms of hydrogen-induced failure are summarized in Appendix B. Generally, the more popular models are the hydrogen induced decohesion of the lattice proposed by Troiano[5]; the adsorption of hydrogen to reduce the surface energy, by Petch[6]; and the accumulation of molecular hydrogen in internal voids and cracks to exert a pressure which lowers the apparent fracture stress, by Zapffe[7].

An anodic and cathodic polarization dependence on time-to-failure (T_f) relationship, has often been used to distinguish the stress corrosion cracking and hydrogen embrittlement phenomena. In Figure 2b, T_f decreases as cathodic currents are imposed and increases with anodic polarization, presumably showing evidence for hydrogen embrittlement. The converse is true in Figure 2c in which case stress corrosion cracking is the proposed cracking mechanism. Combinations, such as Figure 2a and 2d, indicate open circuit cracking according to stress corrosion cracking or hydrogen embrittlement mechanisms, respectively.

Although it was initially considered that a dual mechanism can be applied to differentiate between stress corrosion cracking and hydrogen embrittlement, (i.e., hydrogen embrittlement at cathodic potentials and stress corrosion cracking at anodic potentials), Truman[8] and later Wilde[9] demonstrated convincingly that hydrogen embrittlement could be the operative mechanism in both potential regimes. That a single mechanism should operate under both conditions is not surprising, since the fractographic evidence showed that crack paths in high strength steels at both anodic and cathodic potentials were very similar.

The electrochemical basis for the above conclusion is the fact that conditions in localized geometries (pits, crevices, cracks, etc.) may be quite different than the smooth surface, as discussed

earlier. In view of the work by Pickering, Frankenthal and co-workers [10-14], it was shown that when a net anodic current flows out of localized geometries in metals, the potential in the cavity is less noble than at the outer surface. This potential gradient is understandable in terms of a high resistance path through the electrolyte in the cavity arising from the constriction caused probably by hydrogen bubbles [10]. Hence, the composition (pH, anion and cation concentrations, etc.) as well as potential in a propagating crack may be quite different from that at the bulk electrode surface, and, in consequence, the reactions occurring at the electrode surface and in the crack tip may also be quite different. In essence, both metal dissolution and hydrogen evolution may occur at a crack tip regardless of the electrochemical potentials imposed at the electrode surface. What this means in terms of the potential dependence of the time-to-failure, Figure 2, for example, is that the same mechanism - whether it be hydrogen embrittlement or stress corrosion cracking - may occur without regard to the applied potential.

The general relationship, that hydrogen embrittlement occurs at cathodic potentials and stress corrosion cracking occurs at anodic potentials, is only true to some extent. The localized geometry of the steel (e.g. cracks, crevices) and the environment actually determine the onset of either corrosion mechanism. It should also be noted that, evolution of hydrogen during crack propagation does not necessarily demonstrate that hydrogen embrittlement occurs. As discussed earlier in the text on the mechanisms of hydrogen embrittlement, the molecular hydrogen which evolves is not detrimental, rather, it is the atomic hydrogen which enters the metal that is the cause for concern in high strength steels.

In summary, it should be considered that the evolution of hydrogen arising from overprotection signifies the availability of hydrogen

at a steel surface. Whether this in turn represents hydrogen embrittlement, would depend on the amount of atomic hydrogen diffused into the matrix and made available at crack initiation sites. The chemical environment, stress state, and the nature and geometry of the surface would be the important determining factors in controlling the diffusion of hydrogen into the matrix.

3. FACTORS INFLUENCING HYDROGEN RELATED CORROSION OF STEEL IN CONCRETE

3.1 Mechanical and Metallurgical Factors

Steel tendon for prestressing usually takes one of the three forms: wires, strands or bars.

In prestressed structural concrete, tendons are 7-wire strands conforming to CSA-G279. The equivalent ASTM specification is ASTM A416, uncoated seven wire stress relieved strands for prestressed concrete. Their tensile strength, in general, is between 1300 and 1900 MPa. Material properties of some of these steels are given in appendix C. Commonly, these materials are cold drawn eutectoid carbon manganese steels. That is, a steel which has been cold worked to achieve its high tensile strength. The hard drawn wire is usually stress relieved by a process of straightening and low temperature heat treatment, in order to improve the various mechanical properties, such as ductility. A further process of stabilization, by simultaneous stretching and heat treating, is sometimes used to improve the stress relaxation properties of the steel. Other types attain high tensile strength by heat treatment, that is by quenching and tempering. However steels fabricated in such a manner, do not conform with CSA G279.

The process used in the fabrication of concrete reinforced with prestressing steel, involves pretentioning the strands, before they are placed in the concrete. After the concrete has reached a predetermined strength, the strands are cut and the prestress force is transferred to the concrete through the bond between the concrete and the strands.

Deformed reinforcing bars are derived from hot-rolled steels with varying carbon content. They are usually required to meet CSA-G30.12. These specifications are strictly mechanical property requirements, and do not closely control the chemistry or manufacturing process of the bars. Bars are usually specified to have a minimum yield strength of 300MPa (Grade 300) or 400MPa (Grade 400). A CSA-G30.16 designation specifies a bar with controlled chemistry that is weldable with a yield strength range of 400MPa to 540MPa. In the case that bars are to be welded, a specific recommended standard CSA-W186, is applied.

According to the current level of knowledge, hydrogen is thought to be situated in either lattice sites or in lattice defects. Hydrogen, present in a metal in the form of a free proton in the lattice, can either diffuse in a lattice or become trapped in lattice defects, such as vacancies and dislocations. The possibility of embrittlement of the metal will depend on the form of the hydrogen and its localization in the interior of the metal. Therefore, the embrittlement does not necessarily increase with the quantity of gas present in the metal, but depends on structural defects and possible interactions between them and hydrogen. Basically, the damaging effects of hydrogen depend strongly on the metallurgical characteristics of the materials itself, i.e. chemical composition, microstructure, strength level, thermal and mechanical history, and others.

Effect of Strength Level

It is a rule of thumb that embrittlement becomes more severe as the strength level increases above 700 MPa, and steels with strengths below 700 MPa show no significant embrittlement. Like

most rules of thumb, these are often true, but there are also exceptions. One reason for the exceptions is that susceptibility to hydrogen is a marked function of composition and microstructure.

The interrelation of strength level and microstructure is illustrated in Figure 3 for a specific Cr Mo steel [15]. In this case, a variation in strength was produced through changes in microstructure due to increases in the tempering temperature after quenching. The reduction in area (R.A.) loss falls steadily as strength is reduced from 1500 MPa to 750 MPa by increasing tempering temperature; but below a strength of 750 MPa the trend is reversed. This occurs because a new microstructure of spheroidized carbides begins to appear at this point. As it becomes better developed and the carbides coarsen, RA loss increases because the microstructure is susceptible to hydrogen. The behaviour below 700 MPa contradicts rules of thumb about strength.

On the other hand, it is important to recognize that the most serious manifestation of hydrogen embrittlement is delayed failure, since this corresponds to a loss in effective strength. The loss in ductility in Figure 3 need not correspond to a strength loss. Delayed failure susceptibility does indeed become rather slight for steels with strengths below 700 MPa. Thus, the rule of thumb contains an important kernel of truth when appropriately interpreted.

Effect of Microstructure

Generally, plastic deformation of a steel increases the total amount of hydrogen which can be introduced into the steel. Besides the trapping of protons by dislocations, hydrogen can be

stored in microvoids induced by cold working and in non-metallic inclusions. These microcracks are usually formed in contact with cementite lamellae.

The role of cold working on the stress corrosion and hydrogen embrittlement behavior is rather ambiguous. Some results showed that plastic deformation improved the performance of the steel, others showed that it had a deleterious effect. Nontheless, for a steel which was homogeneously cold worked prior to hydrogen charging, a reduction of the hydrogen embrittlment effect was found.

Generally, carbon steels and high strength steels hardened by cold-drawing, are more resistant to hydrogen embrittlement and stress corrosion cracking than the same steels hardened by quenching and tempering[16,18]. However, data available are relatively sparse, compared to studies on quenched and tempered steels, particularly for actual and simulated concrete environments.

The reason that a cold drawn carbon steel shows a better resistance to hydrogen embrittlement, is that hydrogen diffuses with greater difficulty toward a zone of high load triaxial stress and causes crack initiation. Alternatively, microvoids, where hydrogen condenses, are preferentially oriented in the as drawn axis[17], which is also the direction of the mechanical stress application in service. Consequently, such microvoids would not become high stress concentration cracks.

The role of microstructure on the effect of hydrogen in steels is complex. However, the main trend is that a refined microstructure [16](be it of a quenched and tempered microstructure; a fine dispersion of spheroidal carbides; or a fine pearlitic spacing),

improves a given steel's resistance to hydrogen embrittlement. Part of this improvement is believed to be associated with the manner by which boundary and lattice carbides and other interfaces trap hydrogen, and whether such traps are innocuous or noxious.

Another important interdependent variable is thermal treatment. Although perhaps the most exploitable variable in terms of obtaining improved properties, it is also the most easily abused. Thermal treatment affects solute partitioning, the nature of traps, and substructural unit size.

Effect of Steel Composition

The chemical composition of an alloy is readily available from the supplier, and can serve as a rough guide to material behavior. However, composition usually tells only part of the story, because other metallurgical variables are also important. For example, a given composition of steel can often be prepared with several different microstructures and corresponding strength levels, which will differ in the extent to which they are hydrogen embrittled. As an example, the addition of manganese to steel tends to be deleterious [19]. This trend is of particular concern because Mn is commonly added to medium strength steels to strengthen the ferrite phase. Figure 4 shows that Mn, in the usual composition range for such steels appreciably reduces the threshold stress intensity K_{th} due to hydrogen (in this case called K_{ISCC}). This deleterious effect of Mn is more pronounced in aqueous solution under cathodic polarization. 4340 steel, though not related to pre-stressing steels, is used as an example in the context of showing the effect due to H_2 embrittlement. For most prestressed steels, carbon, manganese and silicon are added because they are inexpensive, and effective strengtheners and

improve hardenability. Sulfur and phosphorus are tramp elements whose presence is usually undesirable, for both toughness of the steel, and for resistance to hydrogen.

The presence of carbon, particularly at the higher-strength levels, has been shown to promote sustained load cracking in an aqueous environment, where hydrogen embrittlement is most probably the cause of the environmentally induced cracking [20]. Carbon apparently reduces the critical stress intensity at the onset of crack growth, and appears to have a deleterious effect in the manifestation of hydrogen damage. Fe-Mn-C steels, especialy as they are driven to higher strength levels by increased alloy additions, are particularly prone to hydrogen embrittlement. Silicon, on the other hand, seems to reduce crack velocities caused by hydrogen, at least in high strength steels [20].

3.2 Environmental Factors

Significant effects on stress corrosion cracking behavior of steels have been observed in aqueous environments with the following variables. Low solution pH, applied cathodic potentials, presence of chloride ions and the addition of cathodic poisons accelerate the failure of samples in aqueous media.

Effect of pH and Applied Potential

The delayed failure of a high strength steel in aqueous media is rapidly accelerated by a decrease of solution pH. Applied potentials, both anodic and cathodic, have been found to accelerate the delayed failure of high strength steel.

The hydrogen induced stress corrosion cracking of precracked specimens of cold drawn concrete prestressing tendon persists from acid conditions up to a pH of about 12.8 [21]. Heretofore this material has been assumed to be immune to SCC at higher pH values. However, McGuinn [22] found that at room temperature and at the free corrosion potential, there exists, in addition to the low pH regime (i.e. up to 12.8) a high pH regime (above about 14.5) for SCC. The width of the immune zone between these two areas appears to be a function of temperature and chloride content (Figure 5) [22].

The electrochemical basis for the above conclusion was found to be true if the test samples had smooth surfaces. In the presence of a crack, as investigated by Brown et al[23], it was shown that the pH measured in the crack tip of a 0.45C (see Carbon Steel - Glossary) steel exposed to aqueous NaCl was 3.8 regardless of the bulk pH. Hence, even though hydrogen production should not occur at the bulk pH and potential, such hydrogen production may occur in the crack tip, provided an appropriate potential is also present in the crack tip.

Effect of Cathodic Poison

Cathodic poisons, containing elements from Group V and VI of the periodic table, have been shown to promote hydrogen entry into iron or steel from aqueous media. Radhakrishnan and Shrier[24] have studied the enhanced permeation of hydrogen through steel as a function of cathodic poison additions to a 0.1N H_2SO_4 solution. Permeation kinetics were increased (during charging) on the addition of As (as sodium arsenite), Se(as selenous acid), and Te. Sulphur compounds were found to enhance permeation kinetics in the absence of an applied potential. The effectiveness of each

poison species, in promoting hydrogen entry, is As>Se>Te>S. Cathodic poison additions have been clearly shown to increase hydrogen entry into high strength steel, in conjunction with lowering the stress required for delayed failure in aqueous media.

Hydrogen sulphide additions to neutral or acidic aqueous environments will strongly accelerate the delayed failure kinetics of high strength steels.

Effect of Chloride Ions

Pourbaix[25] devised a compact summary of thermodynamic data in the form of electrical potential versus pH diagrams, which includes the electrochemical and corrosion behaviour of iron in an aqueous medium. Figure 6 indicates that iron is in a passive state at a pH in the range of 8 - 13. This accounts for the protective properties of concrete and the absence of steel corrosion in concrete when no chloride ions, or only small amounts, are present. A careful inspection of Figure 6 indicates, however, that corrosion may begin if the pH of the system is raised above 13. In this case, a soluble ferrite, $HFeO_2^-$, forms. Any mechanism where iron dissolves at an appreciable rate in concrete can be considered serious corrosion. Thus, addition of materials that further increase the pH of concrete may be detrimental.

For concrete containing chloride, the modified diagram shown in Figure 6 should be used. In Figure 7, which might apply as a general phenomenon to concrete containing chlorides, another corrosion area has been indicated, designated as 'pitting'. This area covers part of the passivation area in Figure 6. In this area, the passivating coating on the steel is broken locally by the chloride present, after which the iron is pitted.

By hydrolysis of the Fe- salts, the pH value in the corrosion pit falls. Simultaneously, the potential E decreases because of the disappearance of oxygen present in the pits. These two effects may result in a condition lying below the hydrogen evolution line. Corrosion in the pit then takes place with simultaneous hydrogen evolution. The occurrence of hydrogen in the corrosion pits explains the possibility of hydrogen embrittlement and the occurrence of brittle fracture in prestressing steel.

In an investigation of A416-74 steel prestressing wires, Griess and Naus[26] found that for bare steel, cracking occurred in NH_4NO_3 solutions above 38°C. However, cracking was not found in <u>any</u> chloride solution, regardless of pH, but cracking was observed at pH<7 in solutions containing H_2S. Treadaway[27] conducted stress corrosion tests on cold-drawn carbon steel wires in concrete containing calcium chloride, and in boiling NaCl of pH 10-11. Although specimens were stressed to ~80% of <u>UTS</u>, no failures were noted after 27 months exposure to the concrete, or 400 hours in the boiling solution. No applied potentials were used, however, and the duration of the exposure in the concrete may have been too short to be definitive. Gilchrist and Nayaron[28] tested cold-drawn wires in sodium chloride containing arsenite as a poison; failures were observed during cathodic polarization at 95% <u>YS</u>. Thus, this data is difficult to interpret in terms of its applicability to concrete service particularly under cathodic protection, and the possibility of problems cannot be discounted.

Most previous investigations of stress corrosion cracking/hydrogen embrittlement of prestressing steels have involved exposure in aqueous solutions. Treadaway[27] had, however, performed experiments upon cold drawn carbon steel stressed to 70-80% of the ultimate tensile strength, both in concrete with and without

$CaCl_2$, and in boiling sodium chloride solutions with a pH in the range of 10.2-11.6. No cracking was observed in any of these environments. Furthermore, subsequent tensile testing of the wires produced ductile fractures; and where corrosion had occurred, fracture was found to initiate at a pit or at a region of reduced cross-section. It has been pointed out [29], however, that none of these specimens were polarized and that the limited exposure duration (27 months) may have been inadequate to cause failures of the type in question.

Effect of Zinc

Contact of prestressing steel with zinc can be considered to be an example of cathodic protection, although the poor conductivity of concrete may render galvanic action to be small. Brachet[30] has investigated the use of galvanized prestressing steel in concrete with good results. No hydrogen embrittlement problems were noted. Conversely, some failures of prestressing steel apparently due to stress corrosion cracking, in England, have been considered due to the presence of either zinc coating or to a zinc containing compound applied to the steel. Thus, the global information appears to be ambiguous regarding the beneficial aspects of zinc.

4. FAILURES DUE TO THE HYDROGEN EFFECT ON STEEL IN CONCRETE

All kinds of prestressing steels have been affected by corrosion. Actual incidents of corrosion are usually associated with an aggressive environment. In a few instances, steel failures could be related to manufacturing defects in the prestressing steel and not to corrosion.

The durability performance of high strength steels embedded in concrete systems was surveyed by Schupack [31] in 1978. It was noted that the reliability of the systems had been excellent over approximately 50 years of experience with the systems. Twenty-eight failures of stress-relieved steel were reported and it was noted that the failures could be attributed to poor design, introduction of corrosive environments, or poor construction of the systems. It was concluded that steels embedded in concrete which are properly detailed and constructed offer excellent durability against corrosion. A survey of the incidence of corrosion of prestressing steel in the USA during the past five years has shown that, of the approximate total of 50 structures in which corrosion of prestressing steel is known to have occurred, 10 cases involved brittle failures of one or more tendons. These affected only isolated areas in each structure and have not been of a catastrophic nature. Considering that about 200,000 tons of prestressing steel per year are used in the U.S., the number of failures reported is considered small. The most widespread corrosion problems in the U.S. today seem to exist in post-tensioned parking garage decks, particularly in areas of the country where calcium chloride is used for winter deicing, and in post-tensioned structures involving unbonded tendons. A number of cases of corrosion, generally with heavy pitting and loss of metal, have been reported, where end anchorage pockets have either been improperly filled or not filled at all, allowing water to

gain access and accumulate inside the plastic sheathing. Several general cases of corrosion of prestressing steel in wire wound pipes and tanks were reported. The principal factors causing these failures were deficiencies in manufacture or in construction, resulting in an insufficient or damaged mortar coat over the wires.

In the U.S., wires in the post-tensioning tendons of the 6.250 ft. Hood Canal floating bridge in Washington State failed about 18 months after the span opened in 1961, according to Great Britain's National Physical Laboratory (NPL) report [31a]. And about four years later, serious failure occurred when 34 wires of a 40-wire group broke. NPL attributes the failures to hydrogen attack.

A limited survey was also made on the incidence of fracture during the last 10 years in Germany [31a]. The most important failure in the field happened in 1980 when the Berlin Congress Hall collapsed 24 years after construction. An opening of the joint and cracking of the joint-concrete between roof slabs and inner ring beam was found. Hydrogen induced stress corrosion cracking of the prestressed wires in the area of the ring beam joint was identified to be the cause of the collapse.

In addition, most publicized failures in Germany were those involving carbonated high alumina cement of high sulphur content[32]. The mechanism of these failures appears not yet to have been established. But it has been reported that the concentration of H_2S released during carbonation of the cement was very low, probably due to its simultaneous oxidation to sulphate, and also that failures occur only as the carbonating front first reaches the steel.

One failure reported in Germany[30] was attributed to improper storage and transportation conditions. In this case, the surface of the prestressing steel was contaminated by sulphides during handling. Two failures of bridge tendons in France and one in Brazil were identified by Lacombe [30] as being caused by hydrogen embrittlement due to the sulphide contained in a "putty" used for leveling the concrete surface at the place of post-tensioning. The reaction of moisture with the sulphide produced H_2S which reacted with the steel to generate hydrogen, causing the embrittlement.

Pipe failures in the Geehi aqueduct[31] were examined and a discussion given of the results of fracture mechanics tests. On the basis of laboratory experience it is not clear that tendons can stress corrode easily in the field, so that no convincing explanation of service failures can presently be given.

Three failures in Argentina showed, that in well designed structures, which are constructed with sufficient care, the necessary conditions for stress corrosion should not occur.

Recent British evaluations, however, have raised again the possibility that hydrogen embrittlement of prestressing steels in concrete structures may indeed be difficult. Failures attributable to hydrogen embrittlement have been noted on the Braidley Road and Scotswood bridges in England, and this failure mode has also been observed at the Hood Canal floating bridge [31a]. In these instances hydrogen embrittlement is attributed to poor protection of the steel in the sheaths, or to no sheathing at all.

Hydrogen embrittlement was alleged to be causing wires to snap in rope hangers on the 3240 ft. Severn Suspension bridge near Bristol. Some scientists said galvanizing was aggravating hydrogen attack of the 15 year old span by creating a steel-zinc corrosion cell.

Monfore and VerBeck[35] and Cornet[36] describe various failures of prestressing steel in concrete, but all instances (except one described by Cornet, apparently due to an H_2S problem) were due to corrosion reducing the load bearing area. No failures were noted by Okada[37] in his survey; thus, problems encountered in prestressed concrete appeared generally to be related to general corrosion and not to stress corrosion cracking. Brachet[30] mentions, but unfortunately does not illustrate, European examples of SCC in prestressing steels. The lack of common hydrogen problems in prestressing is supported by information from Griess and Naus [38], who surveyed data from the nuclear industry where prestressed tendons are used in containment vessels. In several instances, pitting was noted where grease protection had failed. In only one case was hydrogen embrittlement noted; here, the humidity control in prestressing ducts, together with the coating on the cables, was found to be inadequate.

Finally, a comprehensive paper by M. Nurnberger[39] was presented describing 242 instances of damage on prestressing steel during the period 1950 to 1979. Such damage is related to bridges, tanks, pipes, roads and building elements.

In view of the 1 million tons of pre-stressed steel which are at present used annually all over the world, the number of reported failures is relatively few.

5. CATHODIC PROTECTION

5.1 Principles of Corrosion of Steel in Concrete

Corrosion of metals is an electrochemical process that involves the passage of electric currents on a micro or macro scale. In the case of steel, the change from the metallic to the ionic form occurs by a reaction at the anodic site, such as

$$Fe \rightarrow Fe^{++} + 2e^{-} \qquad (1)$$

while at the cathodic site, depending on the pH, either one of the following reactions can occur:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad (2a)$$

$$2e^{-} + 2H^{+} \rightarrow (2H)_{atomic} \rightarrow H_2 \qquad (2b)$$

Under open circuit conditions, the potential associated with the former (eqn.1) is approximately -850mV (CSE), while for the latter (eqn.2) this value is near +400mV (CSE). The net driving voltage for current to flow is then 1250mV.

On connecting the external circuit between the anode and the cathode, current flow is encouraged. In this case, corrosion occurs at sites where the current is from the metal into the electrolyte, and these locations are termed anodes. Thus, all metal surfaces are comprised of microelectrodes (small anodes and cathodes), and the current which flows between these causes corrosion. Because the relative polarity of such surface electrodes varies with time, uniform corrosion results. In the case of steel in concrete, polarity variations that occur over distances of several meters or more, may be possible.

While cell potential constitutes the driving force of corrosion, kinetic factors are largely determined by polarization. And it is this latter phenomenon, which is most influential with regard to corrosion rate. Thus, it has been determined that the potential of an electrode is a function of the net current flowing through it. For open circuit conditions (no net current flow), the potential of the iron reaction was stated to be -850mV (CSE) and of the oxygen reaction +400mV (CSE). When current flows, however, the potential of the anode and the cathode are represented by a pair of curves, as shown in Figure 8. For a corrosion exposure involving a low resistance electrolyte, the metal surface will be nearly equipotential. The point on the polarization diagram, where these conditions are fulfilled (equipotential and equicurrent) is that of Φ_{corr}. This parameter, Φ_{corr}, also designates the potential of the metal. The corresponding net current which flows between anodic and cathodic sites is I_{corr}, and corrosion rate is directly proportional to this (Figure 8).

In situations involving finite resistance either through the electrolyte, as is likely to be the case with steel in concrete, or through an external electrical connection or both, an IR or voltage drop exists as is shown in the polarization diagram in Figure 9. In this case, only a fraction of the open circuit voltage is available to serve as the driving force for current flow, as reflected by the potential difference between anode and cathode.

It is recognized that corrosion occurs at sites where current (positive) flows from metal into the electrolyte. On the other hand, if cathodic current is provided by an external source to the metal, then the net anodic current is reduced or eliminated altogether.

This is illustrated in Figure 10, where cathodic polarization ranging from free corrosion to complete protection is illustrated. Complete protection is achieved, then, when the metal is polarized to the reversible or open circuit potential of the anode (ϕ_{Fe} in Figure 10). No additional benefit is derived from polarization to a more negative potential. Disadvantages of over protection are (i) that additional cathodic current is required, (ii) that any coating on the metal may become disbonded and (iii) that hydrogen damage of the metal may result. The latter is particularly significant in the case of high strength steels, as employed in prestressed concrete.

The corrosion of conventional reinforcing steel in otherwise protective concrete can usually be traced to the action of chloride ion, either added originally to the concrete, released from constituents of the concrete, or applied to the concrete surface by deicing salt or by sea water. Macrocell action between steel in different areas of the structure is considered an important mechanism of such corrosion. However, one of the most important mechanisms of failure of prestressed concrete, is the unexpected brittle failure of the high-strength prestressing material. This can be considered to be due to the phenomenon of hydrogen embrittlement. The mechanism of this type of failure in high strength steels is generally considered to be due to entry into the steel of hydrogen from the corrosion reaction.

The concept of cathodic protection applied to conventionally reinforced concrete bridge decks is an accepted method of halting deterioration of the structure due to chloride-induced corrosion of the embedded steel and this method is being considered for application to other reinforced concrete structures. Many structures, however, contain high strength prestressing steel in addition to the conventional reinforcing steel. While the

application of cathodic protection to such structures may halt general or localized corrosion of the prestressing steel, it raises the possibility of initiating hydrogen embrittlement of such steel.

Essentially, cathodic protection is a means of controlling the corrosion of metal structures by altering the electrical potential of the metal so as to restrict the flow of positively charged metal ions away from the metal.

The cathodic protection of conventional reinforcing steel, the techniques which may be used, and the criteria for cathodic protection levels which may be applicable, have been discussed[40]. The two common techniques of cathodic protection are the galvanic (sacrificial) anode technique and the impressed current technique.

In the impressed current system, which is a commonly employed technique, DC current from an external power source is forced from an outside anode through the concrete to the rebar. This is shown schematically in Figure 11[41]. Concerns about this technique are the electrical continuity in existing structures and over-protection. Rebar continuity is essential in order to protect all the steel. Without continuity, the current can jump from rebar to rebar causing interference thus creating anodes out of some of the rebar (stray current corrosion).

Over-protection could result in H_2 embrittlement. As the current flows from the anode to the cathode, a thin layer of hydrogen forms on the steel surface. Too little current will not protect the steel and too much (H_2 bubbles form at the steel surface at -1170mV (CSE)) risks hydrogen embrittlement of the rebar, particularly in high strength prestressing steel.[42]

5.2 Cathodic Protection of Prestressed Steel

A commonly used criterion for the application of cathodic protection to bare steel is to polarise the steel to a potential of at least -850mV (CSE)[43]. However, for reinforced concrete structures, it may be that a less active potential would be sufficient due to the presence of an already protective environment. One common practice used for protecting reinforced concrete structures is to depress the potential of the steel reinforcement by an arbitrary amount of 100mV to 200mV[44] from the rest or free corrosion potential. Since the free corrosion potential for steel, which is corroding in deteriorated concrete, may be of the order of -620mV (CSE), depression of the potential by 200mV would involve polarising the steel to a potential of -820mV (CSE). King et al[45] have argued that this would be a dangerous practice, because, in the presence of chloride ions and at high values of pH, polarisation to potentials between -810mV and -910mV (CSE) would place the steel in the general corrosion region of the Pourbaix diagram. In order to test this hypothesis they attached steel plates to concrete blocks of varying permeabilities and immersed them in artificial sea water. After exposure in this environment at various constant potentials they found that severe corrosion of the steel plates occurred at potentials between -810 mV and -910mV (CSE). Other workers, however, using mainly simulated environments [46,47] reported that polarisation to potentials more negative than about -780mV (CSE) arrested corrosion of the steel strands possibly because of the thickening of the magnetite film which could be responsible for the continued passivation below -780mV (CSE). Scott[48] has shown that steel with a damaged concrete cover can be protected by polarization in a range from -710mV to -810mV (CSE), and a minimum value of -500mV was specified.

In an experimental investigation by Cherry and Price [49], it was found that a potential more negative than -460mV (CSE) may be sufficient to protect the steel in concrete against corrosion.

Caution must be exercised in cathodic polarization of steel in concrete, since at potentials of approximately -1100mV (CSE), and more negative, the cathodic reaction can result in evolution of hydrogen gas at the metal-concrete interface[50]. A number of research studies have shown that a reduction in bond strength may accompany this. In the case of steel tendons in prestressed concrete, hydrogen embrittlement may arise.

Criteria for the cathodic protection of reinforcing steel in concrete are vague[40]. In many cases, either a standard "pipeline" protection criterion of -850mV (CSE) is used, or a protection level corresponding to the lack of corrosion on Corrosometer^{R} probes attached into the reinforcing steel network, are utilized. Laboratory evaluations have suggested that different potentials may be used to protect steel in concrete, depending on whether corrosion has already been initiated or not. Thus, Hausmann[51] suggests that a protection potential of -500mV (CSE) is acceptable in the first instance, but that -710mV (CSE) is necessary in the second. Vrable[52] has shown that cathodic protection is achieved irrespective of prior exposure at a value of -770mV (CSE), and that this potential protects against pitting as well as general corrosion. Vrable also indicates that visible hydrogen evolution occurs on steel in concrete at a potential of about -1170mV (CSE).

Laboratory studies [53] of the electrochemical behavior of steel reinforcement in simulated concrete environments, with and without chloride ion, demonstrated that corrosion can be controlled by the application of cathodic current to corroding steel. Under all

conditions tested, it was found that corrosion was stopped at a steel polarized to a potential of -770mV. Bond studies showed that the application of a cathodic-protection current to rebars in concrete can result in a decrease in bond strength between the steel and the concrete. Evaluation of the results, in relation to the anticipated conditions of cathodic protection applied to a bridge deck, indicates that the decrease in bond strength would be slight and would not give reason to reject the use of cathodic protection on bridge decks. The results show that over-protection of steel in concrete should be avoided.

Therefore, the major factor regarding over-protection of conventional reinforcing steel during cathodic protection has been steel/concrete bond deterioration, a factor which appears not be be of major concern until potentials exceed -1000mV(CSE). Since Vrable has suggested that visible hydrogen evolution did not occur in a simulated concrete environment until a potential of -1170mV(CSE) is reached, this value cannot be relied on as an arbiter of possible hydrogen embrittlement problems. Thus, at the current state of knowledge it would appear that the use of the least active potential commensurate with cessation of corrosion activity on either electrically connected reinforcing steel, or on the prestressing steel itself, is the prudent course to follow.

A simplified relationship between the electrical potential of a cathodically protected metal structure and the applied current per unit of surface area (current density) is shown in Figure 12[54]. The slope of the plot is a function of the physical and chemical characteristics of both the concrete and the steel, and reflects the nature of the environment in which the steel/concrete combination is exposed.

Further work is undoubtedly necessary to augment present knowledge of the effects of cathodic protection on prestressing steel in concrete. This work should include the determination of a proper cathodic protection criteria for prestressing steels.

6. CONCLUSIONS AND RECOMMENDATIONS

In view of the information compliled in the previous chapters, it is conceived that there are numerous factors contributing to hydrogen embrittlement in prestressing steel. These factors are summarized and discussed briefly as follows:

6.1 Mechanical and metallurgical

Of the many variables which determine the response of materials to hydrogen, most are metallurgical and mechanical in nature, such as chemical composition, microstructure and strength level. These variables and their interrelation are described in detail in Chapter 2. In summary, the following points should be noted.

- Strength Level - It is considered, that as a rule of thumb, steels with strength exceeding 700MPa, are more susceptible to hydrogen embrittlement. Naturally, some of the prestressing tendons fall into this category.

- Microstructure - Since CSA G279 does not permit the use of quenched and tempered products, prestressed steels used are cold worked to achieve the desired high strength. It has been generally accepted that the highly work-hardened steels utilized in prestressing and post-tensioning are much less susceptible both to SCC and hydrogen embrittlement than the quenched and tempered counterparts.

- Composition - Carbon, though considered to promote sustained cracking, is present in prestressing steels in content as high as 0.9%.

Variables like microstructure and strength cannot be treated independently. In fact, it is likely that all hydrogen effects on fracture behavior are ultimately traceable to microstructural details. Composition, for example, merely sets limits upon the microstructures which can be produced in a material. Regarding the variables as independent is useful, however, because composition and strength level are much more readily characterized than are microstructural details. Furthermore, the relevant microstructural details which control the numerous and complex manifestations of hydrogen embrittlement are as yet rather imperfectly known. Thus, the most practical approach incorporates the overall type of microstructure, together with composition, strength and processing history, to identify relative susceptibilities to hydrogen.

6.2 Environmental

Corrosion of prestressing steel may start before it is embedded into concrete. This could occur as a result of an accumulation of dust from chemically aggressive soils or splashing with liquids at a construction site (e.g. deicing salt). The Joint Committee of RILEM-FIP-IABSE states "that the probability of occurrence of corrosion fractures of periodically wetted tensioned prestressing steel is slight, but electrolytes liable to promote pitting may find their way onto the surface of the steel. Consequently, it is required to take particular precautions in handling the prestressed steels".

It has been considered that the deterioration of prestressed steel can occur in the presence of chlorides, since this type of steel corrosion would take place starting with the formation of pits. Subsequent chemical reactions would lead to the evolution of

hydrogen which may partialy or fully penetrate into the steel. Therefore, a good quality chlordie free concrete, correctly produced, will provide an environment in which degradation will not occur.

Other types of ions which have been proven to be detrimental to steels are SO_4^-, S^{2-}, NO_3^- and NH_4^+. [55,56]

Both low and high solution pH, and applied potentials have been found to accelerate the delayed failure of high strength steel. The presence of cathodic poisons such as As, Se, Te and S, which promote hydrogen entry into high strength steel, should be avoided.

From the material's standpoint, it is a fact that high strength prestressing steel is susceptible to hydrogen embrittlement. High tensile strength and high carbon concentration are both considered to promote the susceptibility of hydrogen embrittlement, even though the cold worked microstructure is considered more resistant to hydrogen embrittlement than the quenched counterpart.

Despite the intrinsic properties of the material, environmental factors contribute significantly to the vulnerability of prestressing steel to hydrogen embrittlement. These factors include the level of pH, and whether there are any chloride ions or cathodic poisons present.

Based on the reported failures and factors influencing hydrogen related corrosion of steel in concrete, it should be considered that the risk of hydrogen embrittlement in highway structures is not high, on condition that the steel used is properly fabricated and handled, and is not exposed to any corrosive environment that would produce H_2 during service.

6.3 Cathodic Protection

Cathodic protection may indeed be used to control the corrosion of prestressing steel. Special consideration, however, must be given to a number of design issues that specifically relate to the metallurgy of high strength steels, and to the structural configuration of prestressed concrete structures.

The criteria for protection of steel embedded in concrete are not clearly defined. Most commonly, corrosion engineers use the potential compared to a standard reference cell as the sole criterion. The criterion for steel that is buried or submerged is normally accepted as -850mV (CSE). However, steel embedded in concrete exhibits more noble potentials than exposed steel, in the order of 200 to 300mV more positive. Therefore, some investigators claim that protection is provided at lower potentials, in the order of -500mV to -700mV (CSE).

The primary concern for the cathodic protection of steel embedded in concrete by an impressed current technique, is the overprotection of steel. Overprotection could result in H_2 embrittlement. H_2 bubbles were found on steel surface when it had been polarized to a potential of -1170 mV (CSE).

It is recognised that the possibility for the embrittlement of metal will depend on the form of hydrogen and its localization in the interior of the metal. The level of embrittlement does not necessarily increase with the quantity of gas present in the metal, but depends on structural defects and possible interactions between these and hydrogen. If a structure has inherent defects which are vulnerable to hydrogen embrittlement, the production of hydrogen from cathodic overprotection, would certainly promote the risk of hydrogen embrittlement of the structure. Due to the

limited data available in the literature, it would be impossible to predict the extent of embrittlement that might be induced by hydrogen generated during cathodic overprotection. It is concluded that more engineering data in this area, is required.

S. H. Lo, Ph.D
Scientist

R. T. Lassau, Manager
Materials Corrosion/
Metals Investigations

0760k

REFERENCES

[1] T.P Hoar and J.G. Hines, Stress Corrosion Cracking and Embrittlement, p.107, Wiley, N.Y., 1956.

[2] A.J. Forty, Physical Metallurgy of Stress Corrosion Cracking, p.99, Interscience, N.Y., 1959.

[3] M. Smialowski, in Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloy, NACE, Houston, TX, 1977, p. 405.

[4] R.A. Oriani and P.H. Josephic, Acta Met., Vol. 25, 2977, p.979.

[5] A.R. Troiano, Trans. ASM, vol.52, p.54, 1960.

[6] N.J. Petch, Phil. Mag., vol.1, p.331, 1956.

[7] C.A. Zapffe and C.E. Sims, Trans. AIME, vol.145, p.225, 1941.

[8] J.E. Truman et al, JISI, vol.202, p.745, 1964.

[9] B.E. Wilde, Corrosion, vol.27, p.326, 1971.

[10] H.W. Pickering and R.P. Frankenthal, J. Electrochem. Soc., vol.119, p.1297, 1972.

[11] B.G. Ateya and H.W. Pickering, Hydrogen in Metals, p.207, ASM, Metals Park, 1974.

[12] H.W. Pickering and P.J. Byre, J. Electrochem. Soc., vol.120, p.607, 1973.

[13] B.G. Ateya and H.W. Pickering, J. Electrochem. Soc., vol.122, p.1018, 1975.

[14] D. Harris and H. W. Pickering, Hydrogen effects on behaviour of Materials, AIME, N.Y., 1976.

[15] J.D. Hobson and C. Sykes, J. Iron Steel Inst., 169, 1951, p.209.

[16] B. Marandet, Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, NACE 5, 1973, p.774.

[17] E. Gasior, Colloque Franco-polonais sur l'hydrogene dans l'acier et la fonte, 1963.

[18] W.O. Everling J. Amer. Iron Steel Inst., 1954, p.185.

[19] A.W. Thompson and I.M. Berstein, Advances in Corrosion Science and Technology (R.W. Staehle and M.G. Fontana eds.), vol.7, Plenum, N.Y.

[20] I.M. Berstein and A.W. Thompson, Int. Met. Rev., vol. 21, 1976, p.269

[21] McGuinn, K.F. and Griffiths, J.R., Br. Corros. J., 1977, vol. 12, p.152.

[22] K.F. McGuinn and M. Aballe, Br. Corros. J., 1982, vol.17, no.1, p.15.

[23] B.F. Brown, C.T. Fujii and E.P. Dahlberg, J. Electrochem., Soc., 116, 1969, p.218.

[24] T.P. Rodhakrishnan and L.L. Shreir, Electrochimica Acta Vo. 11, p.1007, 1966.

[25] Poupbaix, M., Atlas of Electrochemical Equilibrium in Aqueous Solutions, Pergamon Press Limited, London, 1976

[26] Griess, J.C. and Naus, J., in Corrosion of Reinforcing Steel in Concrete, ASTM STP 713, p. 32. ASTM, Philadelphia, PA, (1980)

[27] Treadaway, K.W.J., British Corrosion Journal, 6, 66 (1971)

[28] Gilchrist, J.D. and Narayan, R., Corrosion Science 11, 281 (1971)

[29] Slater, J.E., Role of Cathodic Protenction in Prevcenting Corrosion of Prestressing Steel in Concrete Structures, paper No. 177 present at Corrosion/83, april 18-22, 1983, Anaheim.

[30] Brachet, M. and Raharinaivo, A., in Stress Corrosion Cracking and Hydrogen Embrittlement of Iron BAse Alloys, NACE 5, p. 766. NACE, Houston, TX, (1977).

[31] Schupack M.J., J. Am. Concr. Inst., 75 [10], 501-10 (1978).

[31a] Segan, E. G., White, D., Socil, D., Morrow, D., and Kurath, P., in "Corrosion Cracking", ed. Goel, V. S., Conference Proceedings, 1985.

[32] Naumann, F.K., and Baumel, A., Archiv fur das Eisenhuttenwesen, V.32, No.2, Feb. 1961, p.65

[33] Leonhardt, F., Prestressed Concrete for the Practice, 2nd Ed., Wilhelm Ernst and Solin, Benlin, 1966, p.45

[34] E. Phillips, Australian Water Resources Council, paper no. 9, 1975

[35] Monfore, G.E. and Verbeck, G.J., J. American Concrete Institute 57, 91 (1960).

[36] Cornet, I., Materials Protection, January, 1964, p.80.

[37] Okada, H., in Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, NACE 5, p.124. NACE, Houston, TX, (1977)

[38] Griess, J.C. and Naus, J., in Corrosion of Reinforcing Steel in Concrete, ASTM STP 713, p.32. ASTM, Philadelphia, PA, (1980)

[39] U. Nurnberger, "Forschung, Strasenban and Strasenverkehrstechnik" (H.308 (1-195) 1980)

[40] Slater, J.E., Criteria for Adequate Cathodic Protection of Steel in Concrete, Paper No. 132, CORROSION/79, Atlanta, GA, 1979

[41] Stratfull, R.F., "Experimental Cathodic Protection of a Bridge Deck. Transportation Research Record, No. 500, TRB, Washington, D.C., (1974)

[42] Schutt, W.R., Proceedings of Conference on Cathodic Protection of reinforced concrete bridge decks, San Antonio, Texas, Feb. 12-13, 1985, p.46

[43] Schwerdtfeger, W.J., J. Res. Nat. Sur. Stds., 1958, 60(s) p.153

[44] Herriksen, J.F., Corros. Sci., 1980, 20. p. 1241

[45] King, R.A., Nabizadeh, H., and Ross, T.K., Corros. Press Control, 1977 (April), p.11

[46] Cherry, B.W., and Price, S.M., Corros. Sci., 1978, 18, p.1091

[47] Hansmann, D.A., Mater. Prot., 1969, 8(10), p.23

[48] G. N. Scott, J. Am. Water Works Assn., 57 (1965) p.1038

[49] B.W. Cherry and S.M. Price, CorrosionScience vol.18, p.1091, 1978.

[50] 'Cathodic Protection for Reinforced concrete Bridge Decks, Laboratory Phase,; National Cooperative Highway Research Program Report 180, Trans. Res. Board, 1975.

[51] Hansmann, D.A., Materials Protection, October, 1969, p.23

[52] Vrable, J.B., :Cathodic Protection for Reinforced Concrete Bridge Decks - Laboratory Phase'. NCHRP Report 180, TRB, Washington, D.C., (1977)

[53] Vrable, J.B., Chloride Corrosion of Steel in Concrete: A Symposium, Chicago, Illinois, June 27, 1976 p.124

[54] G.K. Chou and K.C. Hover, Concrete International, Design and Construction, vol.9, No.1, p.26, 1987.

[55] Treadaway, K., Brit. Corro. J., 6[3], 66-72, 1971

[56] Gouda, V.K., Azim, A.A. and El-satedm H.A., Corro. Sci. 9[6], 215, 1979

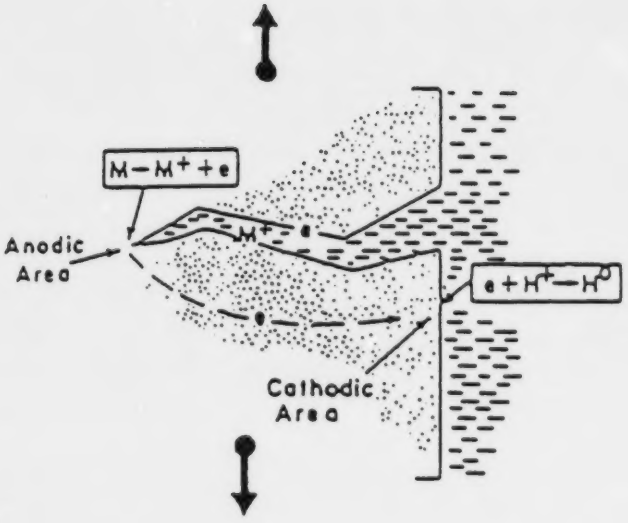

Fig. 1a

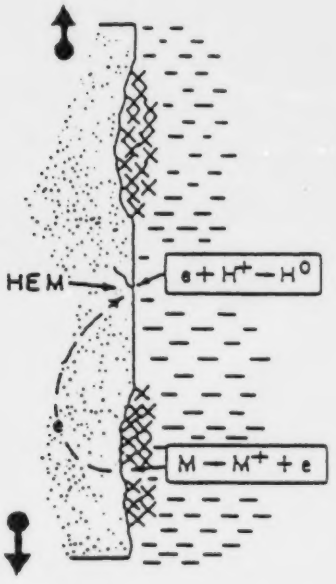

Fig. 1b

Fig. 1 Schematic of cracking by Stress Corrosion Cracking (SCC) and Hydrogen Embrittlement (HEM) mechanisms. (after Wilde (9))

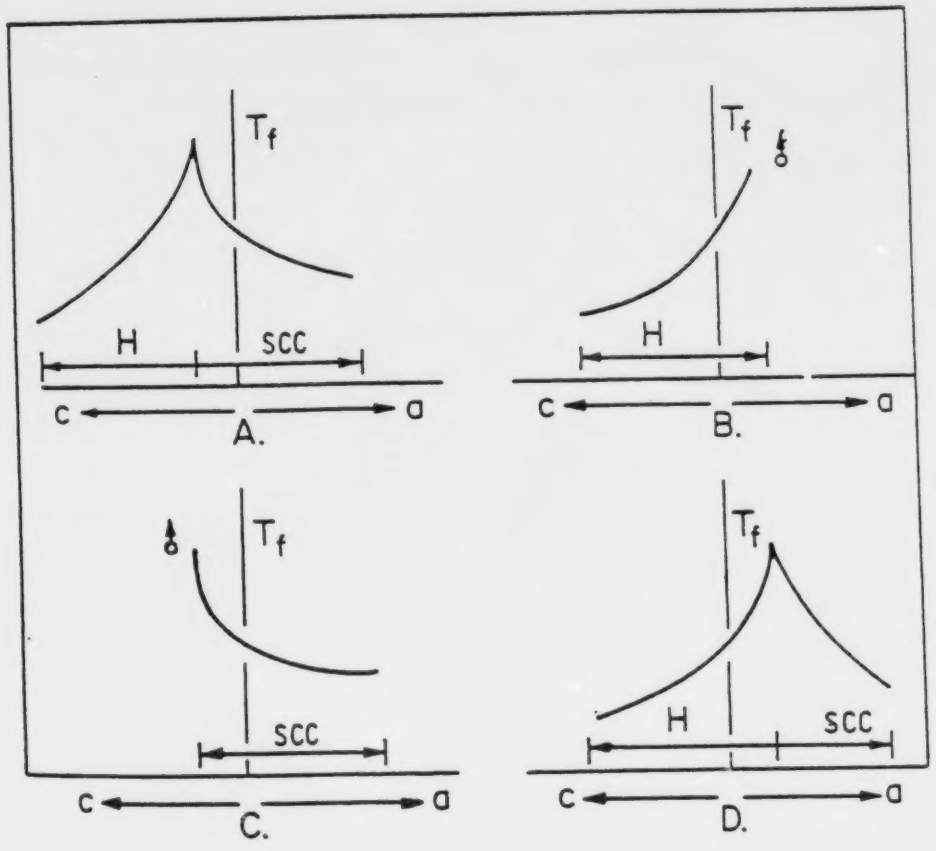

Fig. 2 Influence of anodic and cathodic polarization on cracking susceptibility. (after Wilde)

SCC - Stress Corrosion Cracking. H - Hydrogen Embrittlement
T_f - Time to Failure
a - Anodic Polarization
c - Cathodic Polarization

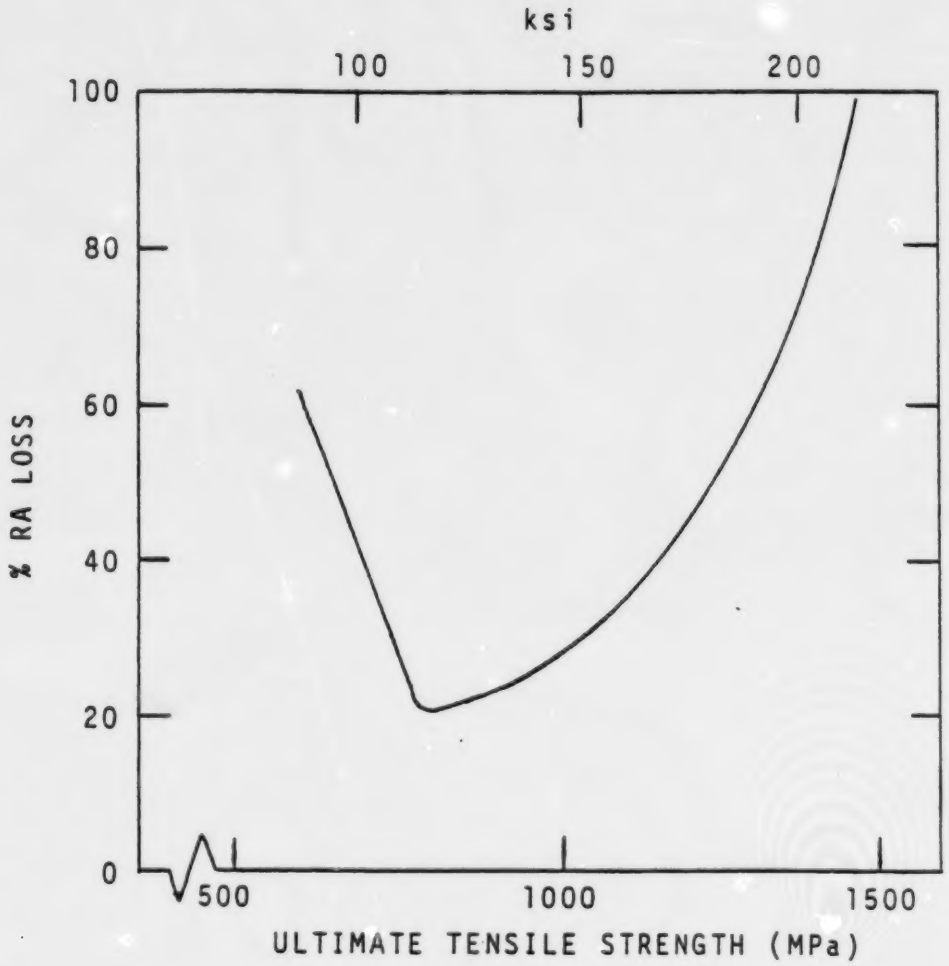

Fig. 3 Ductility (RA) loss as a function of strength level in a 3.3 % Cr, 0.4 % Mo, 0.26 % C steel containing 3.6 wt ppm H. Changes in strength obtained by tempering to produce different microstructures.

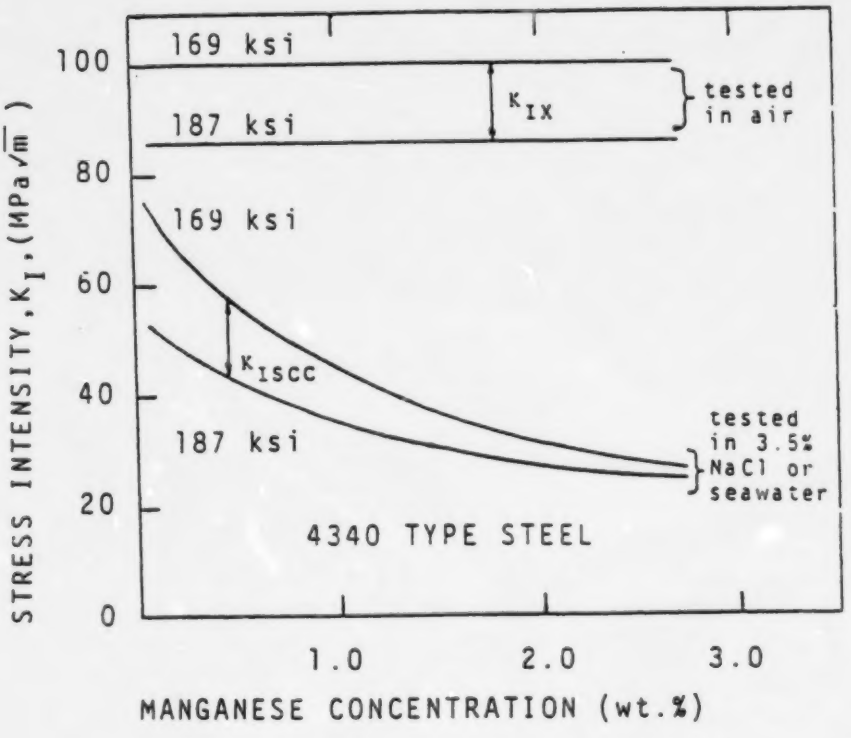

Fig. 4 Effect of manganese on the environmental resistance of 4340 type steel .

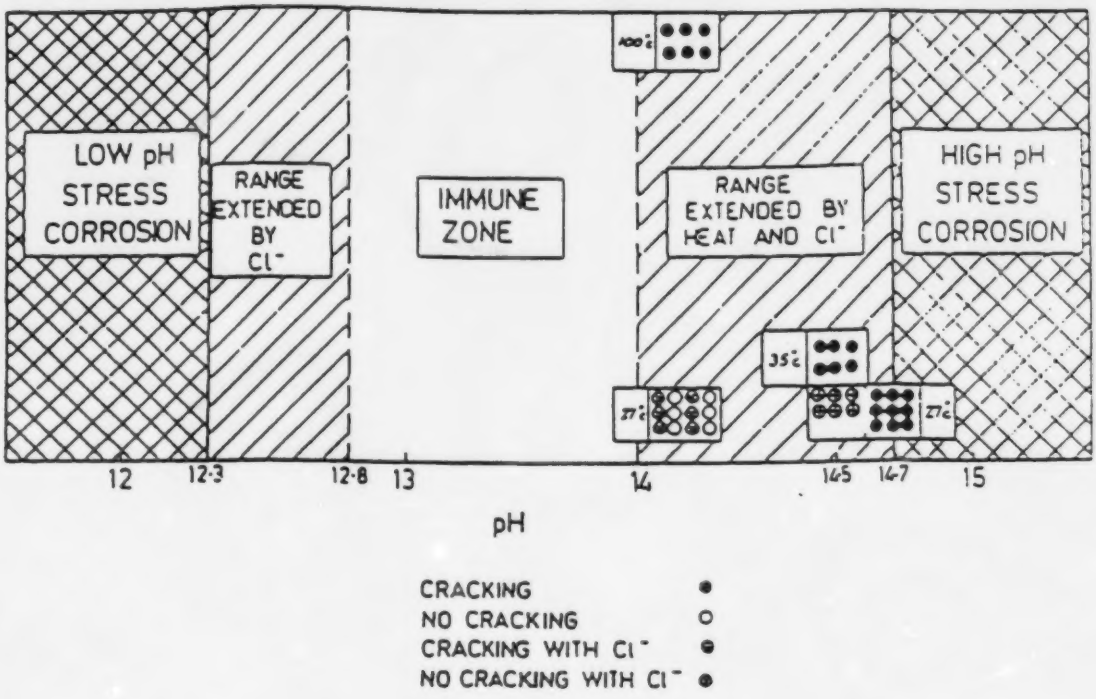

Fig. 5 High and low pH regimes for stress corrosion.

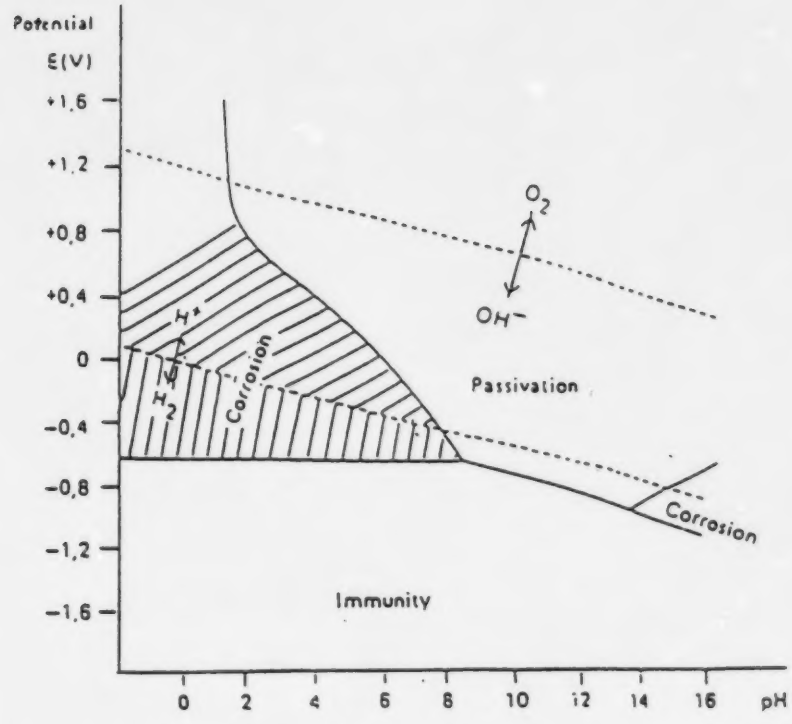

Fig. 6 Pourbaix-diagram for an iron/water system at 25° C.

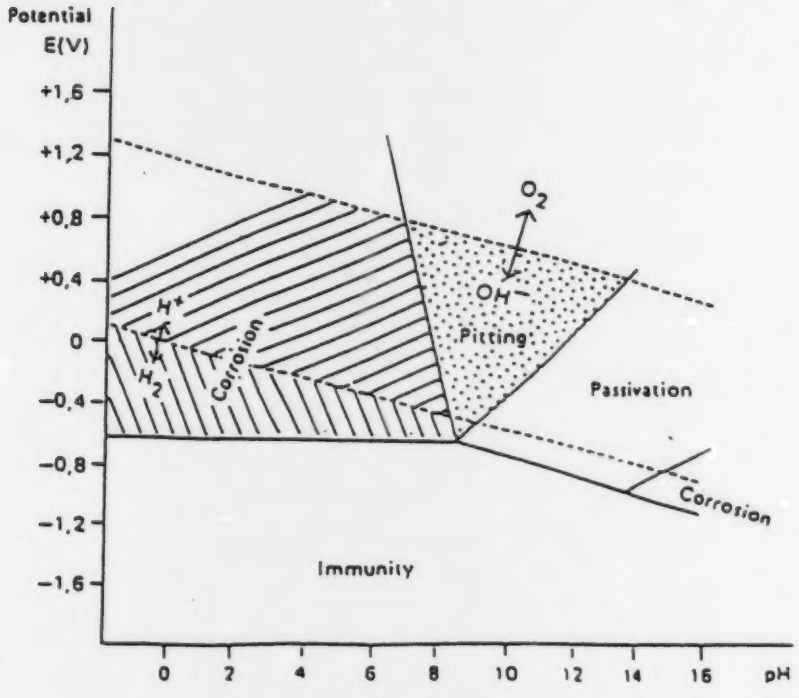

Fig. 7 Pourbaix-diagram for an iron/water system with chloride .

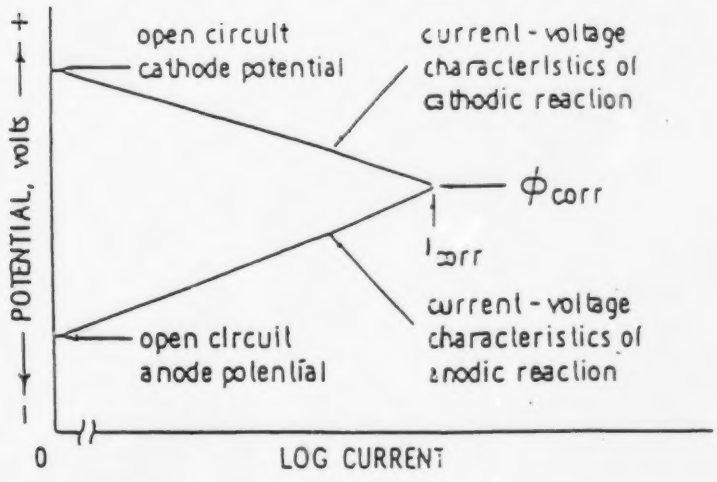

Fig. 8 Polarization diagram illustrating plot of current as a function of potential for an anodic and cathodic reaction.

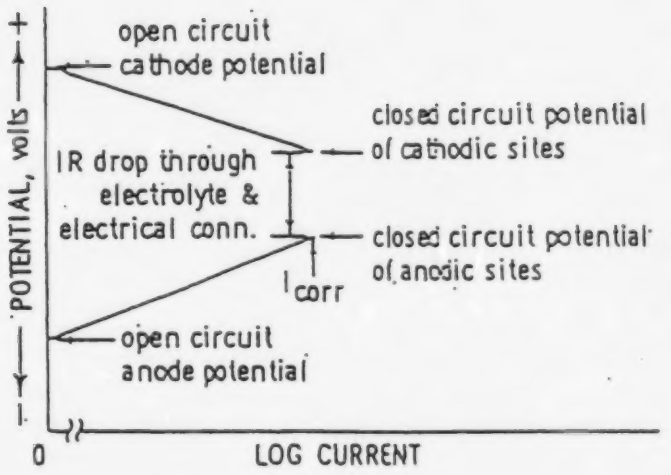

Fig. 9 Polarization diagram illustrating plot of current as a function of potential in a high resistance electrolyte .

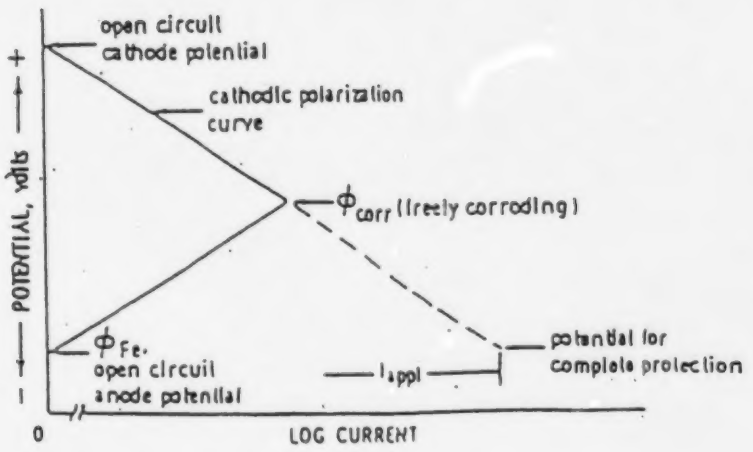

Fig. 10 Polarization diagram illustrating how successive levels of cathodic polarization reduce the anodic current and thereby lower corrosion rate .

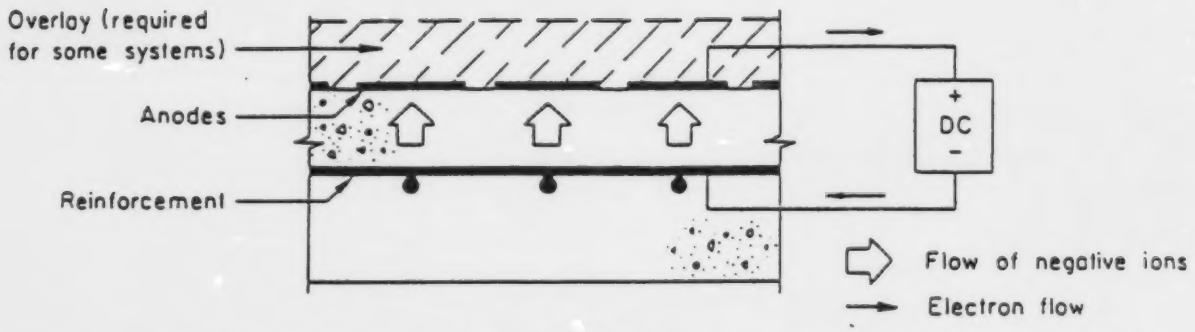

Fig. 11 A cathodic protection circuit alters the electrical potential and restricts the flow of positively charged metal ions away from the metal.

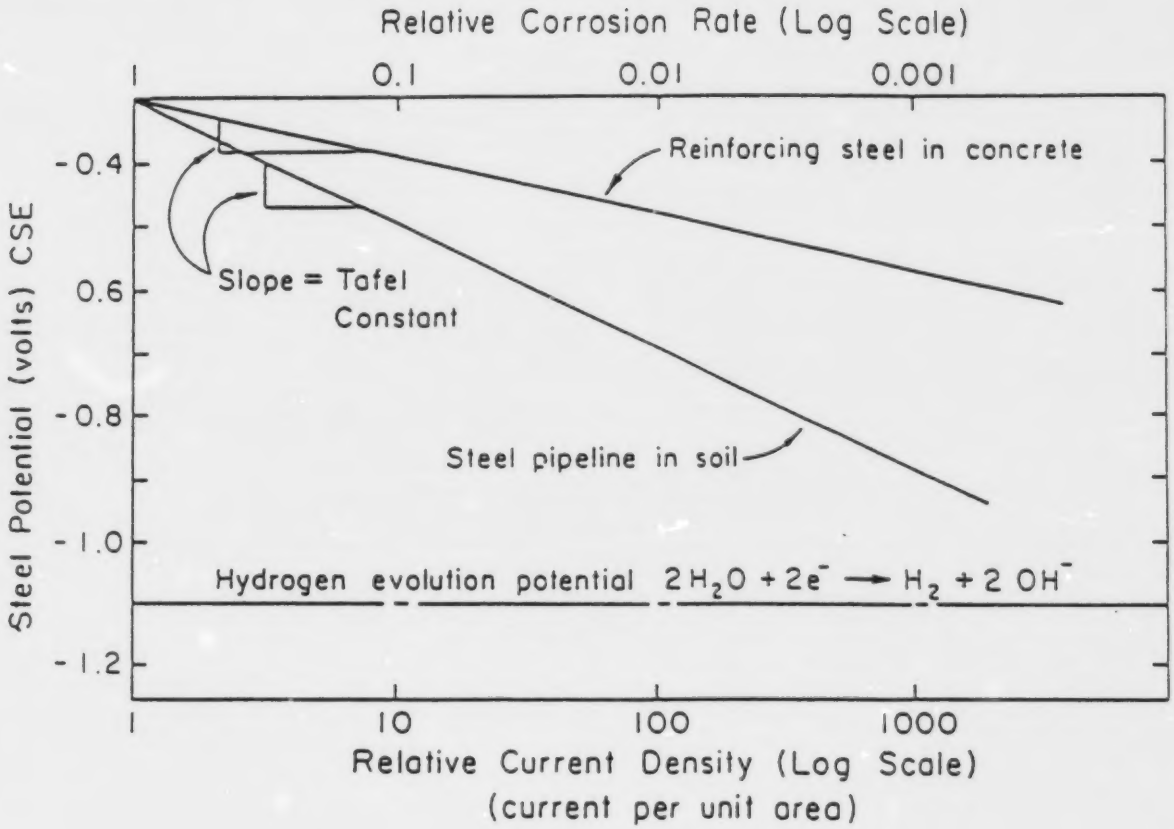

Fig. 12 The relationship between current density and steel potential can be used to operate and control a cathodic protection system to obtain a satisfactory reduction in the corrosion rate.

Appendix A

Stress Corrosion Cracking

Stress Corrosion Cracking

Stress Corrosion cracking can be described as an intergranular (ISCC) or transgranular (TSCC) cracking of metallic materials due to the simultaneous action of a corrosive agent and of tensile stresses. In a recent review [A1], it has been argued that intergranular and transgranular stress corrosion cracking generally occur by basically different mechanisms. It is considered that, with a few possible exceptions, ISCC can be accounted for by the film-rupture model [A2,A3], also referred to as the slip-dissolution model [A4]. The corrosion cracking mechanism essentially operates by preferential anodic dissolution of film free metal at the crack tip, which is exposed by localized plastic deformation.

Surface films in the models include absorbed layers, films of corrosion and reaction products. These films influence the overall stress corrosion cracking mechanism by inhibiting the anodic or cathodic part of the chemical process; influencing the absorption or evolution of hydrogen; and altering the mechanical properties or the local stresses in the surface layers of the substrate metal.

The presence of a film alone, however, is not sufficient to cause stress corrosion cracking. If the environmental conditions are such that any metal exposed by the cracking of the surface film is rapidly passivated, then stress corrosion cracking is not observed. In this case the crack does not have the opportunity to propagate. On the other hand, if the repassivation of the exposed metal is too slow, then the dissolution leads to a blunting of the crack. The consequent reduction in the stress concentration factor, mitigates the stress corrosion cracking. The conditions under which stress corrosion is detrimental are those in which the

passive film is only moderately stable, and a finite amount of metal dissolution is required before repassivation occurs.

The proposed mechanism involves the attack of a localized area of metal which causes the formation of a groove. This very small exposed anodic area carries a very high current density, resulting in a high rate of removal of metal. The high concentration factor of the groove, promotes further localized deformation in the tip of the groove when stressed, thus exposing corrosion prone metal beneath the passive film. The immediate formation of passive film is also required, to localise the anodic attack at the tip of the crack and to prevent the walls of the crack being generally attacked, which would lead to crack broadening and blunting. A model of these three conditions is shown by Staehle in which the significance of the dissolution process is indicated (Figure A1).

The rate of repassivation may be expressed in terms of the following quantities: In Case (I), the reformation rate of the film is so rapid that virtually no incremental propagation of the crack is possible . In case (III), the extent of metal dissolution is so great resulting in a blunting phenomenon. Only in case (II) is the dissolution sufficient, but not too extensive, for a continued crack propagation to operate.

The chemical breakdown of passive film is made easier by the presence of mechanical stress in the film or the substrate. This may be an aspect of the interaction of chemical and mechanical influences upon the properties of the passive film which has been overlooked, and which could lead to an interpretation of the induction period for the initiation of stress corrosion cracking, and of pitting[A5]. The existence of zones of cracking in a current-potential diagram has been extensively documented. Essentially, corrosion cracking can be related to the three zones

in a current-potential diagram, as shown in Figure A2. The zones 2 and 3 bound a region of passivity; above zone 3 is a region of pitting; between zones 1 and 2 is a region of generalized attack; and below zone 1 is a region of cathodic protection.

There has been considerable discussion about the interpretation of the influence of polarization upon the time to failure of a given combination of material and environment [A6]. It has been suggested that if anodic polarization reduces the time to failure, the process must be stress corrosion cracking, whereas if cathodic polarization reduces the time to failure, the phenomenon must be hydrogen embrittlement.

If the corrosion product film which forms on the surface of the metal grows thick, as in the case with brasses, the rate of crack propagation can be shown to be related to the thickening of the film [A7]. The crack only propagates through the brittle tarnish layer and stops at the substrate which is relatively ductile. The crack is thus propagating in a brittle phase which is constantly growing ahead of the crack tip, where its thickness is least.

The above case, basically describes the fracture mode of TSCC. Essentially, TSCC is thought to occur discontinuously by a series of limited brittle-fracture (cleavage) events. The characteristics of TSCC are considered to be best explained by a bulk-embrittlement mode, Figure A3, but the cause of embrittlement has not been established.

The view that TSCC occurs by cleavage, is based in part on the nature of the fracture surfaces. Transgranular fracture surfaces, in virtually all alloy systems, are characterized by a series of parallel crystallographic facets separated by steps which are generally crystallographic in appearance. Of particular

importance, is that the opposing fracture surfaces are matching and interlocking, a characteristic which is fully consistent with cleavage but which cannot be reconciled with a dissolution process. The conclusion that TSCC occurs discontinuously stems from the observation of markings on the fracture surfaces which are considered to represent successive positions of the crack front, and from the occurrence of discrete acoustic emission during propagation.

The crack-arrest markings are not generally resolvable, but appear under certain conditions in a number of systems [A8,A9]. Specifically, the markings are detected in specimens tested under constant load in regions near the transition to ductile overload, and in specimens tested at slow strain rates.

With the exception of Al Alloys [A10], markings of this type have not been detected on intergranular stress corrosion fracture surfaces. Similarly, discrete acoustic emission is not detected during ISCC, although experimental evidence is somewhat limited.

In view of the above models, surface films of corrosion products play an important part in the phenomenon of stress corrosion cracking. For stress corrosion cracking to be severe, it appears necessary for a highly protective thin film to be formed with a minimum of accompanying metal dissolution. On the other hand, a film which provides little protection will probably give rise to more general corrosion attack.

The models so far put forward have apparently not taken account of the fact that the passive films themselves appear to be more susceptible to chemical breakdown when they are stressed. As chemical breakdown of these films is known to take considerable time, this may account for the incubation period observed in stress corrosion cracking phenomena.

[A1] A. J. Bursle and e. N. Pugh, Environment-sensitive Fracture of Engineering Materials, TMS-AIME, Warrendale, PA, 2979, p. 18.

[A2] F.A. Champion, Symposium on Internal Stresses in Metals and Alloys, Institute of Metals, London, 1948, p. 468.

[A3] H. L. Logan, J. Res. NBS, Vol,.48, 1952, p. 99.

[A4] R.W. Staehle, The Theory of Stress Corrosion Cracking in Alloys, NATO, Brussels, 1971, p. 223.

[A5] A.J. Bursle and E.N. Pugh. Mechanisms of Environment Sensitive Cracking of Materials, The Metals Society, London, 1977, p. 471.

[A6] G. M. Scamans, Met. Trans., Vol. 11A, 2980, p. 846.

[A7] E.N. Pugh, Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys, Nace, Houston, TX, 1977, p.376.

[A8] A.J. Bursle and E.N. Pugh, Mechanisms of Environment-Sensitive Fracture of Engineering Materials, TMS-AIME, Warrendale, Pa., 1979, p. 18.

[A9] A.J. Bursle and E.N. Pugh, Mechanisms of Environment Sensitive Cracking of Matrials, The Metal Society, London, 1977, p.471.

[A10] G.M. Scaman, Met. Trans., Vol. 11A, 1980, p. 846.

Appendix A

Figures

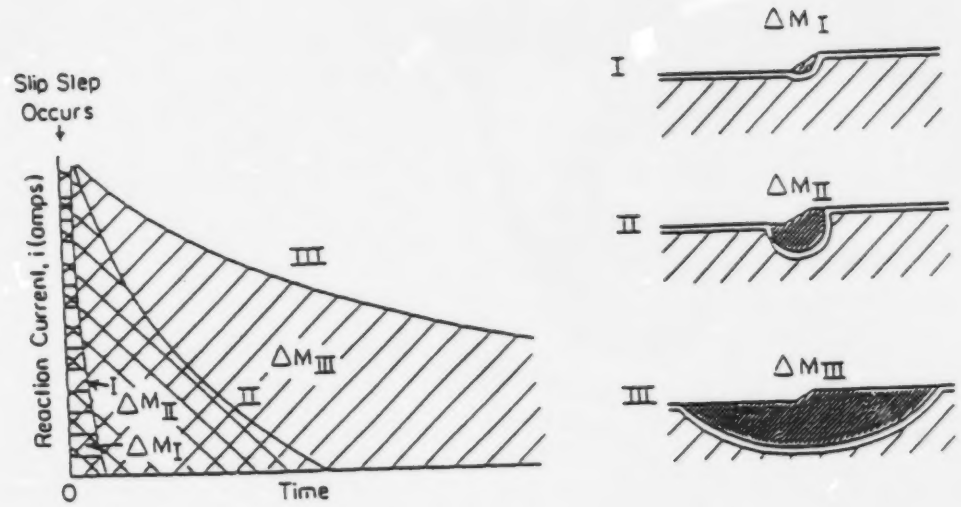

FIGURE A1 – Schematic figure illustrating relationship between current versus time transient, and amount of material dissolved for given slip step event. Case I—rapid repassivation. Case II—intermediate repassivation – favors stress corrosion cracking. Case III—extensive or nonrestricted lateral dissolution.

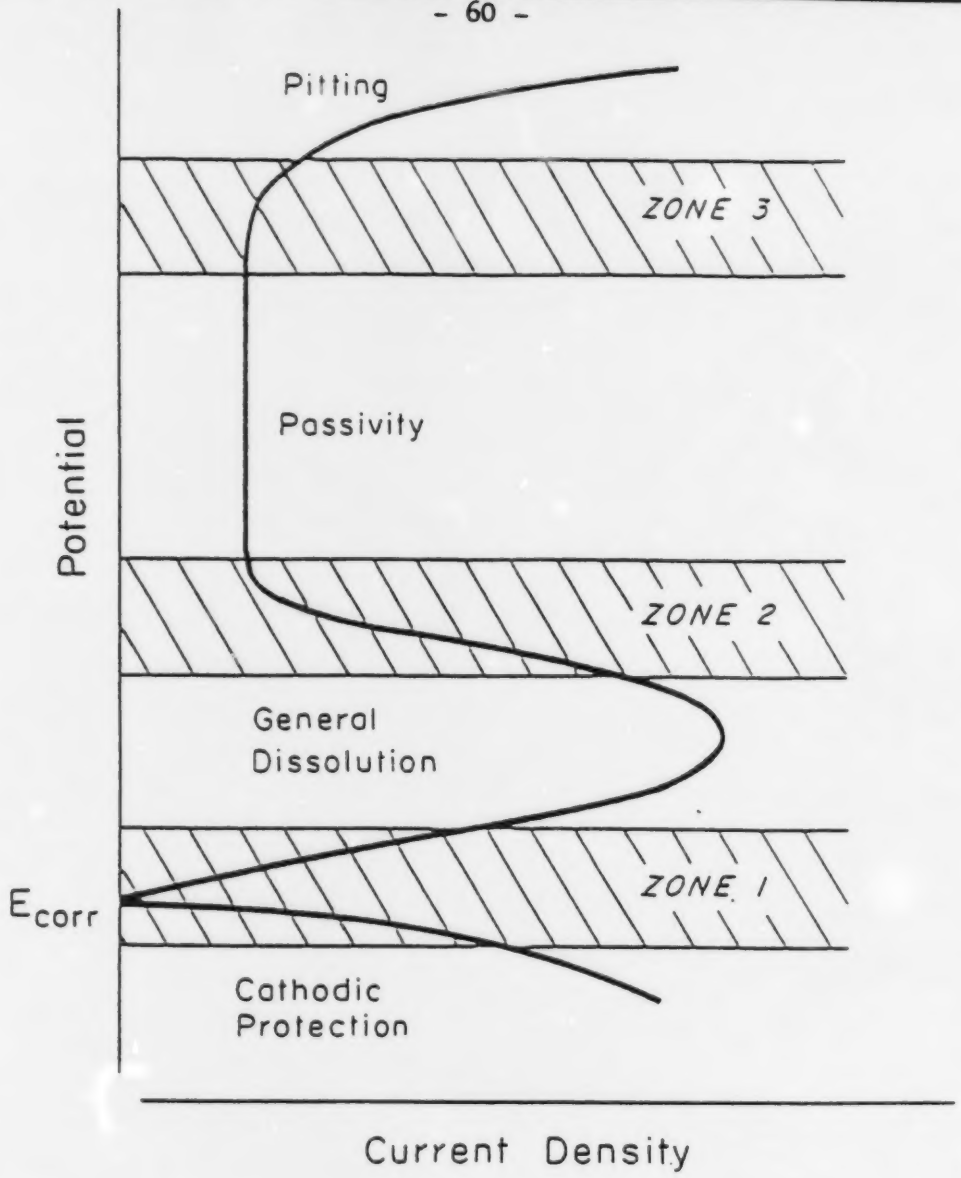

FIGURE A2 – Schematic diagram illustrating positions of Zones 1, 2, and 3 for stress corrosion cracking on polarization curve.

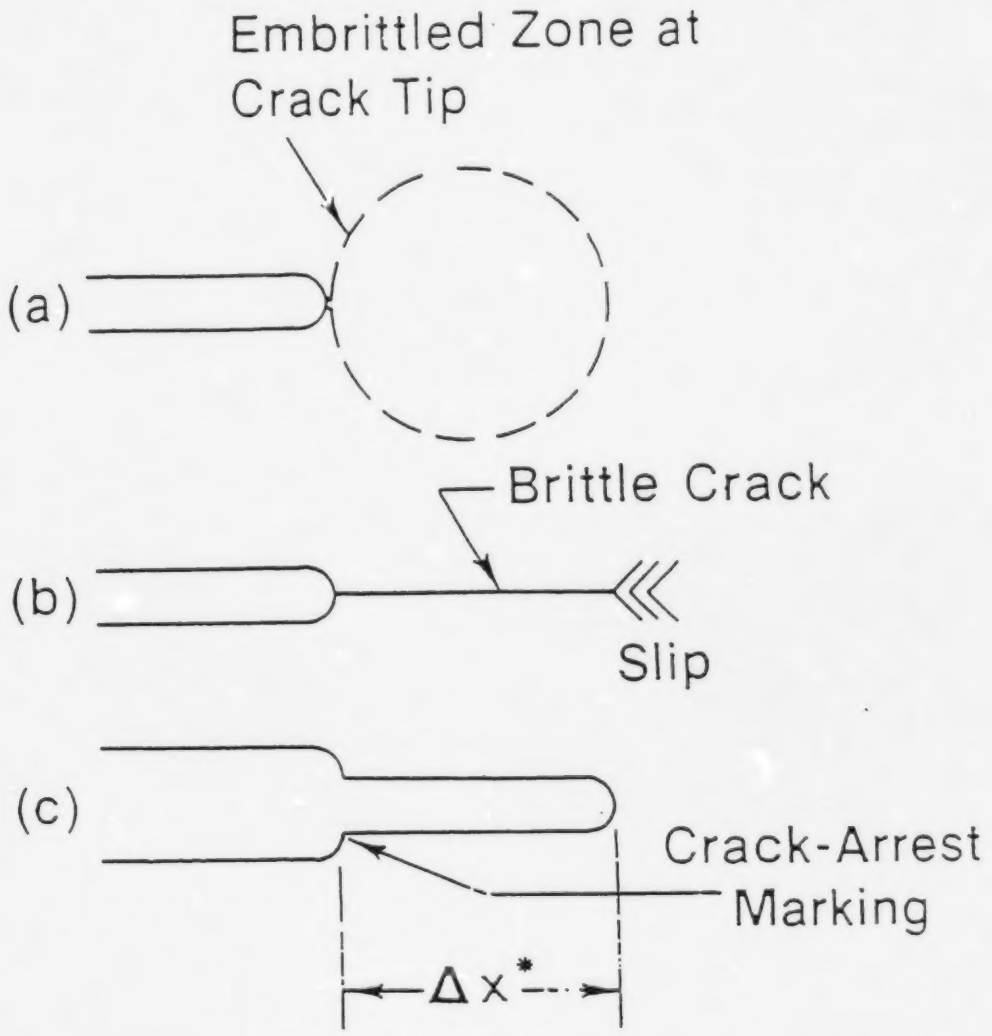

Fig. A3 Schematic of the bulk-embrittlement model for transgranular SCC. It is considered that the lattice ahead of the stationary crack front becomes embrittled by interaction with the solution, permitting the initiation of a cleavage crack. The latter is thought to be arrested by plastic deformation when it emerges from the embrittled region, producing a crack-arrest marking on the fracture surface. The crack is thought to propagate discontinuously by repeated cycles of this process.

Appendix B

Hydrogen Embrittlement

Hydrogen Embrittlement

At the present time, there is little agreement on the different mechanisms that have been proposed to explain hydrogen embrittlement. Whether a hydrogen embrittled crack initiates on the surface, as discussed previously, or initiates in the bulk, is still a controversy. At this point, some of the widely discussed mechanisms will be summarized.

Johnson and Troiano [B1,B2], deduced a model from the results on high strength steels, which suggested that hydrogen in the lattice is the damaging species. The presence of hydrogen can actually reduce the cohesive strength of the base metal bond. The model includes the concept that hydrogen in solution interacts with the electrons of the host metal to lower the binding energy. The hydrogen atoms in the metal matrix of the notched specimen, are believed to be attracted to the point of maximum hydrostatic stress, and subsequently cause embrittlement failure at that point.

In the pressure theory model, the hydrogen degradation is achieved by the increase in hydrogen concentration within internal voids or fissures, creating a large internal pressure which enhances void growth and crack propagation. This phenomenon certainly occurs, for example, in blister formation [B3]. However, the observations [B4] of stable crack growth in dry hydrogen gas, as well as in chlorine and other gaseous environments [B5], shows that the pressure theory is not general.

Contrary to the latter conclusion, it had been suggested that dislocation transport could create large internal pressures in voids even when the source of hydrogen was at low pressure[B6]. However, the theoretical estimates of the internal pressure over-estimated the arrival rate of hydrogen and under-estimated

the departure rate [B7] from voids, and so greatly over-estimated the pressure buildup. It appears that only small super-saturations relative to the hydrogen source can be achieved by dislocation transport [B7]. When the source of hydrogen is at high pressure, on the other hand, internal pressure enhancement by hydrogen transport [B8] is an important process and can contribute to void growth as observed experimentally [B9].

Petch and Stables [B10] proposed that the role of hydrogen is to absorb on the free surfaces created by crack propagation, thereby decreasing the work of fracture and enhancing cracking. Arguments against this model are that it under-estimates the work of fracture; that it cannot account for the reversibility of degradation, for example in delayed failure; and that it cannot account for discontinuous crack propagation. The reversibility of delayed failure could still be related to reduction of surface energy if the latter primarily influenced crack nucleation. Then, not only would surface energy be important but also local stresses associated with dislocation pile-ups and elastic incompatibility, all of which can recover when external stresses are removed.

If hydrogen is to cause internal crack nucleation, it must be transported through a solution phase, absorbed, transported internally by diffusion or dislocation motion, and accreted at a site such as an internal interface where it influences nucleation and growth of a crack. Enhanced transport by dislocations [B11,B12] and decreased transport because of trapping [B13] have been demonstrated. While important in contributing to the degradation process, these phenomena are not by themselves mechanisms but rather they contribute to the overall mechanism [B14].

Birnbaum and co-workers [B15] have shown that transition metals can suffer hydrogen degradation by a mechanism of formation of a hydride phase at a crack tip, cracking of the hydride, and crack arrest and deformation when the tip reaches the matrix phase, the sequence then repeating. Even in circumstances where the hydride is unstable in the absence of stress, it can be stabilized by the hydrostatic tensile field ahead of a mode I crack. For iron, no hydride was found on exposure to hydrogen pressures of up to 2.5 GPa [B16], so the hydride model has not been widely considered for this case. However, calculations have been performed for the Fermi-Dirac atmosphere of hydrogen attracted to the elastic field of a sharp crack tip [B17] in iron at room temperature. High concentrations of hydrogen were estimated to be attracted to the crack tip. Thus, in a very localized region near the crack tip, the Birnbaum process is feasible.

The above models and findings show no one simple theory explains all hydrogen degradation phenomena. The overall process instead, can include as components, many of the above list of mechanisms. In the more general sense, the decohesion theory of Troiano [B18] and others [B19,B20], does encompass most of the observed phenomena. This includes both the weakening of resistance to shear in glide planes, and at free surfaces or void surfaces, where dislocation injection occurs, as well as the weakening of atomic bonds in a reversible or irreversible manner at a propagating mode I crack tip.

[B1] Troiano A.R., Trans. ASM 1960, Vol. 52, p.54

[B2] Johnson, H.H., Morlet J.G. and Troiano, Trans. IMS AIME, 1952, Vol. 212, p.528

[B3] D.P. William and H.G. Nelson, Met. Trans., 1970, Vol. 1A p.63

[B4] R.P. Gangloff and R.P. Wei, Met. Trans., 1977, Vol. 8A, p.1043

[B5] P.W. Kaw, R.W. Ure Jr. and J.G. Byrne, Phil. Mag. 1979, Vol. 39, p. 517

[B6] J.P. Hirth, Relation between structure and strength of metals and alloys, Her Majesty's Stationary Office, London

[B7] H.H. Johnson and J.P. Hirth, Met. Trans., Vol. 7A, 1976, p.1543

[B8] J. K. Tien, A.W. Thompson, I.M. Bernstein, and R.J. Richards, Met. Trans., Vol. 7A, 2976, p.821

[B9] R.I. Garber, I.M. Bernstein and A.W. Thompson, Scripta Met. Vol.10, 1976, p.341

[B10] N.J. Petch and P.Stables, Nature, Vol. 169, 1952, p.842

[B11] J.A. Donovan, Met. Trans., Vol. 7A, 1976, p.145

[B12] J.K. Tien, A.W. Thompson, I.M. Bernstein, and R.J. Richards, Met. Trans. Vol. 7A, 1976, p.821

[B13] G.M. Pressouyre and I.M. Bernstein, Met. Trans., Vol. 9A, 1978, p.1571

[B14] S.P. Lynch, Metals Forum, Vol. 2, 1979, p.189

[B15] S. Gahr, M.L. Grossbeck, and H.K. Birnbaum, Acta Met., Vol. 25, 1977, p.125

[B16] B. Baranowski, Ber. der Bunsen-Gesellschaft, F. Phys, Chem., Vol. 76, 1972, p.714

[B17] I.M. Berstein and A.W. Thompson, Inst. Met. Rev., Vol.21, 1976, p.269

[B18] A.R. Troiano, Trans. ASM, vol. 52, 1960, p.54

[B19] R.A. Oriani and P.H. Josephic, Acta Met., Vol. 25, 1977, p.979

Appendix C

Material Properties of Prestressing Steels

MATERIAL PROPERTIES
PRESTRESSING STEEL

Fig. 8.2.3 Properties and resistance of prestressing strand, wire and deformed bars

Seven Wire Strand						
Grade f_{pu}	MPa	1860				1760
Size Designation		9	11	13	15	16
Nominal Diameter	mm	9.53	11.13	12.70	15.24	15.47
Nominal Linear Mass	kg/m	0.432	0.582	0.775	1.109	1.173
Nominal Area A_{ps}	mm²	55	74	99	140	148
$0.7\ f_{pu}\ A_{ps}$	kN	71	96	128	182	182
$0.8\ f_{pu}\ A_{ps}$	kN	81	110	147	208	208
$f_{pu}\ A_{ps}$	kN	102	138	184	261	261

Prestressing Wire					
Grade f_{pu}	MPa	1550	1720	1620	1760
Size Designation		5[1]	5	7	7
Nominal Diameter	mm	5.00	5.00	7.00	7.00
Nominal Linear Mass	kg/m	0.154	0.154	0.302	0.302
Nominal Area A_{ps}	mm²	19.6	19.6	38.5	38.5
$0.7\ f_{pu}\ A_{ps}$	kN	21.2	23.6	43.6	47.4
$0.8\ f_{pu}\ A_{ps}$	kN	24.3	27.0	49.9	54.2
$f_{pu}\ A_{ps}$	kN	30.3	33.7	62.3	67.7

Deformed Prestressing Bars							
Grade f_{pu}	MPa	1080	1030	1100	1030	1100	1030
Size Designation		15	26	26[2]	32	32[2]	36
Nominal Diameter	mm	15.0	26.5	26.5	32.0	32.0	36.0
Nominal Linear Mass	kg/m	1.44	4.48	4.48	6.53	6.53	8.27
Nominal Area A_{ps}	mm²	177	551	551	804	804	1018
$0.7\ f_{pu}\ A_{ps}$	kN	133	397	424	579	618	734
$0.8\ f_{pu}\ A_{ps}$	kN	153	454	484	662	707	839
$f_{pu}\ A_{ps}$	kN	191	568	606	828	884	1049

[1] Available with surface indentation [2] Available on special order

Glossary

Carbon steel - Steel containing carbon up to about 2% and only residual quantities of other elements except those added for deoxidation, with silicon usually limited to 0.60% and manganese to about 1.65%. Also termed "plain carbon steel", "ordinary steel" and "straight carbon steel". 0.45C is steel containing 0.45% carbon.

Cementite - A compound of iron and carbon, known chemically as iron carbide and having the approximate chemical formula Fe_3C. It is characterized by an orthorhombic crystal structure. When it occurs as a phase in steel, the chemical composition will be altered by the presence of manganese and other carbide-forming elements.

Cold Working (hardening) - Deforming a metal plastically at a temperature lower than the recrystallization temperature to increase its hardness and strength.

Dislocation - A linear defect in the structure of a crystal. Two basic types are recognized, but combinations and partial dislocations are most prevalent. An "edge dislocation" corresponds to the row of mismatched atoms along a straight edge formed by an extra, partial plane of atoms within the body of the crystal, that is by a plane of smaller area than any other parallel section through the crystal. A "screw dislocation" corresponds to the highly distorted lattice adjacent to the axis of a spiral structure in a crystal, the spiral structure being characterized by a distortion that has joined

normally parallel planes together to form a contiuous helical ramp winding about the dislocation as an axis with a pitch of one interplanar distance.

Eutectoid - (1) An isothermal reversible reaction in which a solid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system.
(2) An alloy having the composition indicated by the eutectoid point an equilibrium diagram.
(3) An alloy structure of intermixed solid constituents formed by a eutectoid reaction.

Inclusions - Nonmetallic materials in a solid metallic matrix.

Stress Intensity K_I - Plane strain fracture toughness. It is a measure of the crack resistance of the material.

Lamellae - A term applied to thin plate or scales.

Quench Hardening - Hardening a ferrous alloy by austenitizing and then cooling rapidly enough so that some or all of the austenite transforms to martensite. The austenitizing temperature for hypoeutectoid steels is usually above Ac_3 and for hypereutectoid steels usually between Ac_1 and AC_{cm}.

Tempering - Reheating a quench-hardened or normalized ferrous alloy to a temperature below the transformation range and then cooling at any rate desired.

UTS - Ultimate Tensile Strength-The maximum tensile stress, that a material can withstand.

YS- Yield Strength-The stress at which a material exhibits a specified deviation from proportionality of stress and strain. An offset of 0.2% is used for many metals.